The Purge and Trap Technique

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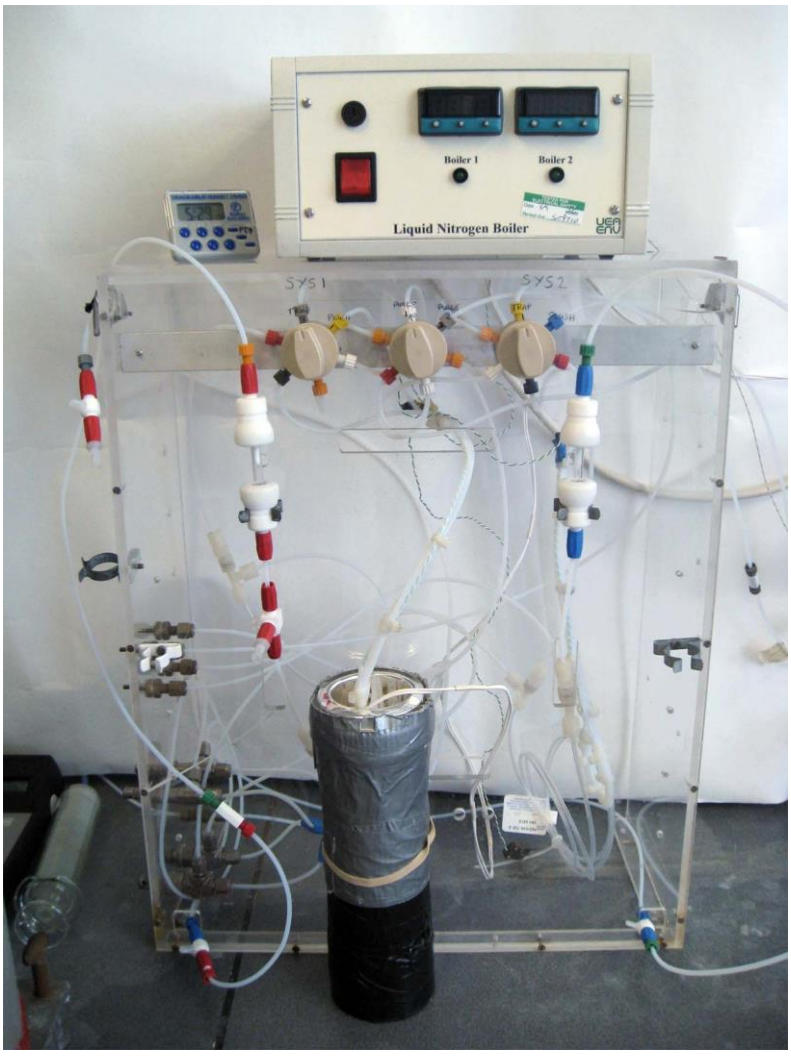
Purge and trap (PnT) is now a commonly used technique for the analysis of volatile trace gases in seawater samples. Traces gases usually occur at concentrations so minute (nM/pM) that they are undetectable by headspace equilibration analysis; which relies on allowing VOC within a sample of water to equilibrate with an enclosed headspace of air, then measuring the VOC concentration with the headspace.

The PnT pre-concentrates the VOC within the sample to a quantity that is detectable by a GC or GC-MS. A stream of Inert gas bubbles (usually nitrogen or helium) are passed through the sample. The VOCs then partition themselves between the aqueous phase and the gas bubbles. The gas bubbles then carry the VOC out solution. The rate at which this occurs and the efficiency of VOC removal will depend on the Henry's law coefficient of the VOC (Chuck et al 2005).

VOCs in the gas stream are then trapped either cryogenically (liquidifying/freezing out) or accumulated on an absorptive material e.g. Tenax (used for DMS/halocarbons).



DMS trapping at Essex

The PnT used at the University of Essex is used for the cryogenic enrichment of DMS (see Photo and Fig 1). It is a twin system with two duplicate analytical systems which operate, and must be calibrated, independently. The set-up is similar to those described by Turner et al (1990) and Vogt et al (2008).

Purge and Traps results can be notoriously unreliable due to the many variables that are being controlled so the procedure must be standardised as much as possible and replicates always taken. Of particular importance are that; the amount of sample added is accurate, a purge flow rate is constant and the purge time is exact.

1) **Apparatus during cryotrapping procedure**.

- N_2 gas from a cylinder (blue line), supplied at XXXX bar, is split into five lines. Two connect with System 1, two with System 2 and the fifth is a spare flow line. Each has one purge flow line ($60ml^{-1}$ min) and one dryer flow line ($150ml^{-1}$ min).
- The purge flow on/off is controlled by a stop valve (B).
- C. When the stop valve is open the purge flow enters the purge tube, where the liquid sample is contained, through a glass frit producing fine bubbles within the sample.
- DMS is degassed from the sample into the N_2 purge flow (now shown in red). The purge flow also picks up moisture from the sample, which must be removed from the purge flow. D.
- Glass wool contained within a glass tube helps to remove some of this moisture and stop any large droplets. E.
- The purge flow then passes a three way switch which adds optional functionality to the system allowing DMS_{air} measurements (see Section XXXX). F.
- A Naflion counter-flow dryer helps to further remove water. The purge flow passes through an inner membrane, surrounding which, the $150ml^{-1}$ min dryer flow moves past it in the opposite direction. Water vapour from the purge flow passes through the membrane into the dryer flow and exits the system as waste (I).
- 'Hex' valve 1 (G)now diverts the purge flow onto the cryoloop (H) which is suspended over a Dewar of N_2(l). A thermocouple on the loop feeds back to a heater block within the N_2(l) to control the temperature of the cryoloop to between -145 to -150^oC using a electrical liquid nitrogen boiler (not shown, built inhouse at UEA, East Anglia).
- DMS has a melting point -98^oC, so freezes into the cryoloop as the purge flow passes through, along with any remaining water vapour.
- The purge flow, now without DMS (darker red), passes back through 'hex' valve 1 and to waste (I).
- In this setup the GC flow line (green line) flows through the 'hex' valves but is not connected to the purge line.

2) **Apparatus during measuring procedure**.

- After a set trapping time (which depends on the volume of sample purged), the stop valve (B) is switched and so is 'hex' valve 1 (G).
- The purge flow stops and the cryoloop is now in line with the GC.

- The cryoloop is then immersed in freshly boiled water and the temperature risen to > 95^{o}C.
- The DMS frozen within the cryoloop evaporates into the GC flow line and is carried to the GC for measurement.
- After 0.4 minutes, all the DMS has been flushed from the trap and valve 1 (G) is switched back to its starting position.

The system is then reset.

- The purge tube is rinsed out with MilliQ water and the purge flow restarted at B.
- Pure N_2(g) now flushes out the whole system.
- The stop valve (G) is then switched again and the cryoloop cooled to between -145 to -150^{o}C ready for the next sample.

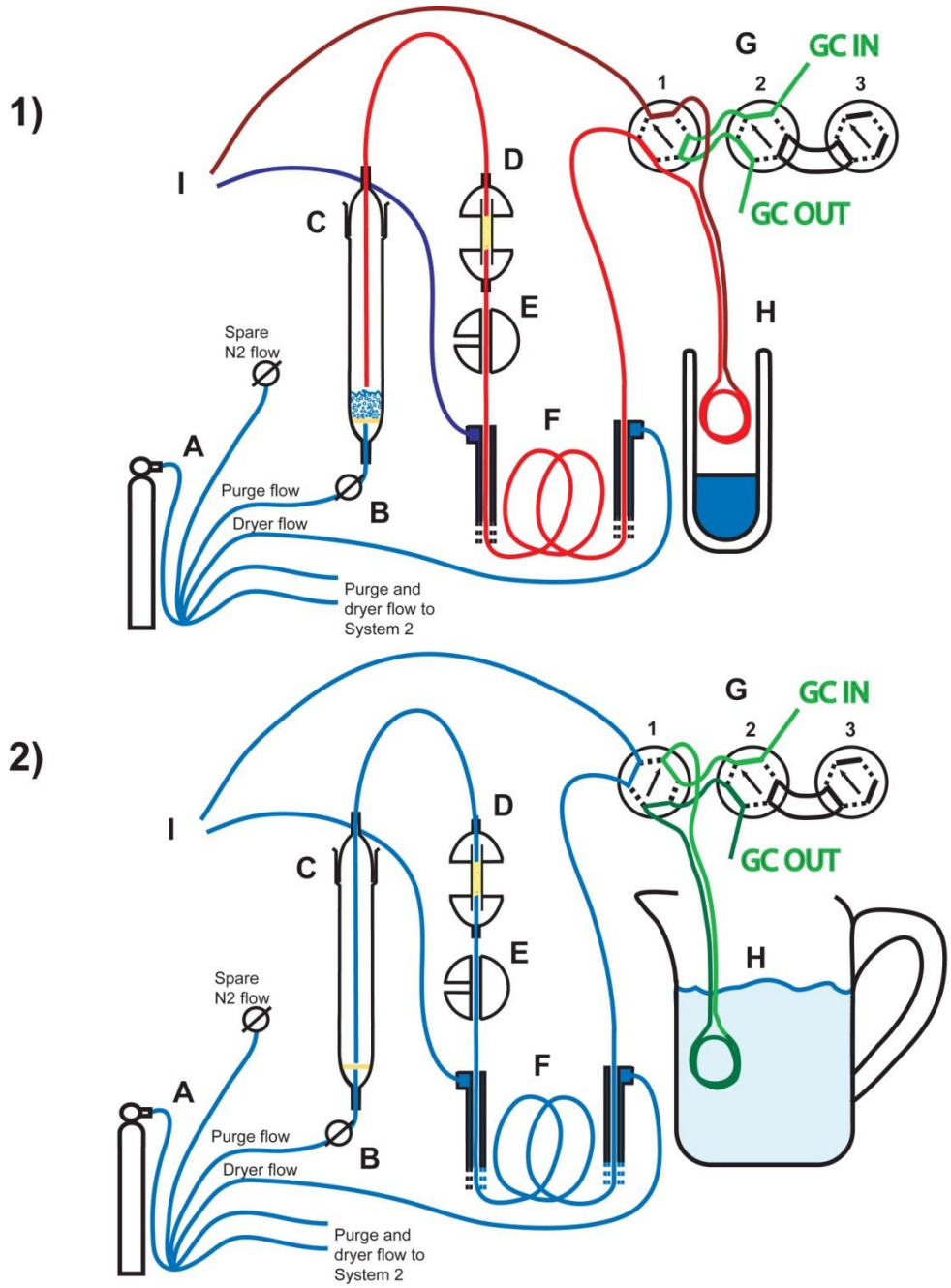


Figure 1. The twin Purge and Trap instrument at the University of Essex. Two analytical systems run independently consisting of:

- A gas supply (A).
- Swaglok valves are used to regulate the gas flow (not shown).
- A stop valve to control flow (B).
- A purge tube where the sample is added(C).
- Glass wool in a tube to catch water droplets (D).
- A three way valve used for Tedlar bag work (E).
- A Naflion dryer to remove moisture from the sample (F).
- A set of 'Hex' valves which direct gas flow (G).
- A cryoloop, which is cooled to between -145 to -155 ^{o}C to trap the DMS (H).
- A set of Waste outflow lines (I).
- The numbers 1) and 2) relate to the set-up during the cryotrapping and flushing procedure (see text).

USING THE PURGE AND TRAP

Preparing System 1 for measurements

- The purge tube and top should be stored in an acid bath. Remove and rinse it with copious MilliQ and reattach it to the purge and trap.
- Twist purge top into purge tube for a tight fit.
- Low gas flow (~5 mL min^{-1}) should always be passing through the system to keep in clean
- Attach the AGM 1000 flowmeter to the waste and turn up the flow till it is at 60mL min^{-1}.
- Check the dryer flow (it should be 150 mL min^{-1}. Adjust if necessary.
- Turn on Liquid N_2 boiler.
- Put heating block in Dewar and fill up 1/3 with N_2(l).
- Make sure 'hex' 1 in set to trap and 'hex' 2 is set to Sys 1.
- Cool the trap to between -145 to -155 ^{o}C by placing it in the Dewar above the N_2(l). Use rolled up blue roll to block up the opening to the Dewar.

Preparing the GC for measurements

- The standard GC method we use is called XXXXXX. With this procedure DMS elutes after 3.3 mins. The oven is held at 60 ^{O}C for 4 minutes before it ramping to XXX over XXX minutes. The whole method lasts xXXX minutes.
- If there are no peaks during the ramp then you can switch to the method XXXXx which has no ramp and so only lasts XXXX minutes.
- Alternatively if a contaminating peak is very close to the DMS peak switch to the slower method XXXXXXXX. DMs then elutes after xXXX mins.

Running a sample for DMS

- We use two different procedures depending on the quantity of DMS present. For a 1 mL sample we purge for 7 minutes while a 10 mL sample is purged for 15 minutes. Also the purge tubes used are of different sizes. Otherwise the procedure is identical.

- Stop the purge flow, remove the purge top and add your sample the purge tube. Measure out your sample to the highest accuracy you can.
- Immediately restart the purge flow and start the count-down.
- Frequently check the purge flow with the flow meter and tweak it to stay at 60 mL min^{-1}. The quantity of DMS removed from the sample depends critically on the bubbling rate so this is very important for reliable, reproducible results.
- Check that the trap stays at the right temperature and adjust if necessary.
- Boil a kettle full of water.

Stopping the sample

- As soon as the timer beeps stop the purge flow.
- Remove the purge top and pour the sample from the purge tube into a waste beaker.
- Start the bubbling and rinse out the purge tube twice MilliQ.
- Get as much water out of the purge tube as possible.

- Reconnect the purge tube and wait 10 seconds to allow all the DMS within the system to be flushed to the trap.

Flushing the sample to the GC

- Switch 'hex' 1 to flush.
- Take the cryoloop out of the Dewar and plunge into the freshly boiled water at the same time as the GC acquisition is started.
- Swish it around for 0.4 minutes.
- Switch 'hex' 1 back to flush.

Preparing for the next sample

- The purge flow should still be running.
- Cool the cryoloop back down again.
- Stop the purge flow, and add the next sample.

Calibration

- The PnT is susceptible to drift (as is the GC) so the calibration should be checked every day (or twice a day if it is being used all day)
- Aliquots of secondary stock at 4.01 µg mL^{-1} of DMSP-HCl are kept in Michael's drawer in the 3.07 freezer. Equivalent to 0.75346 µg S mL^{-1} or 22.322 nM DMSP.

1ml calibration

- Seven calibration standards are prepared ranging from between ca 0.75 – 15 ng S ml^{-1} (Table 1)
- Vortex mix the standards before use.
- Fresh standards each day.

Table 1. 1mL PnT Calibration standards are made by adding 5 mL MilliQ into a 15 mL centrifuge tube along with a set quantity of DMSP stock.

Standard	**2^{O} stock of DMSP (µl)**	**Sulphur ng mL^{-1}**	**nM DMSP**	**ρmol DMSP mL^{-1}**
0 (Blank)	0	0	0	0
1	5	0.753	0.0235	0.1174
2	10	1.504	0.0469	0.2345
3	20	3.002	0.0936	0.4681
4	40	5.980	0.1865	0.9324
5	60	8.934	0.2786	1.3931
6	100	14.774	0.4607	2.3036

- Pipette 50 µL of 10 M NaOH into the purge tube followed by 950 µL of a standard, purge for 7 minutes.
- The quantities of Sulphur/DMSP within each purge are shown in Table 2 (0.95x values in Table 1

Table 1. Amount of DMSP/sulphur during a purge using 0.95 mL of each purge stock with 50 µl of 10 M NaOH

0.95mL of standard purged	**Sulphur ng in 1ml purge vol**	**nM DMSP in 1ml purge vol**	**ρmol DMSP in 1ml purge vol**
0 (Blank)	0	0	0
1	0.715	0.0223	0.1115
2	1.429	0.0446	0.2228
3	2.852	0.0889	0.4447
4	5.681	0.1771	0.8858
5	8.487	0.2647	1.3234
6	14.035	0.4377	2.1884

Maintenance

- Replace the glass wool daily or if it is visibly wet.

- Cable ties holding the cryoloop are prone to breakage and need regular replacement.
- The cryoloop should have six cable ties at the top of the loop where they are less prone to breakage.
- Changes in the number or position of these ties affect the quantity of DMS trapped (Mann-Whitney $p<0.05$, $n=8$).

Problems

- **Blockages**
- usually caused by ice within the cryoloop.
- Causes the flowmeter to show no flow and the bubbling within the purge tube slows.
- The build up of pressure can cause the purge top to pop out.
- Sample is lost. Heat up loop within boiling water to free blockage.
- Turn the purge flow up to ca 150 mL min^{-1} and leave emersed within the boiled water for 5-10mins.

- **Purge top stuck**
- Tap the junction between the purge tube and top lightly with a spanner. Will loosen.

- **Droplets of water within tube between purge top and glass wool**
- Stop immediately.
- Replace glass wool and replace section of tube.

- **Large contaminating peak**
- Contamination comes from the other sulphur compounds which become trapped within the Naflion dryer membrane and are slowly released back into the purge stream.
- Rinse out entire system with Acid-MiiliQ-alkaline-MilliQ-ethanol-copious MilliQ.
- Repeat if necessary.
- Place system in the drying cupboard with a constant N_2(g) flow.
- Will be ready to use again next day.

Purge and trap cheat sheet

- Balance gas flows, check hex 1 set to trap.
- Stop purge and load sample.
- Start purge and wait for required time (7 or 15 minutes).
- Boil water.
- Stop purge.
- Clean purge tube.
- Start purge and wait 10 secs.
- **'Hex' 1 to flush,** submerge trap and start acquisition.
- After 0.4 mins 'Hex' 1 to trap.
- Cool trap, stop purge and load next sample.